

## Effect of post treatment temperature and humidity conditions on fixation performance of CCA-C treated red pine and southern pine

Guo AiLong(郭爱龙)\* P. A. Cooper

Faculty of Forestry, University of Toronto, Earth Science Center, 33 Willcocks Street, Toronto, Ontario Canada M59 3B3

**Abstract** Rates of fixation in chromated copper arsenate (CCA-C) treated red pine (*Pinus resinosa* Ait.) and southern pine (*Pinus* spp) sapwood specimens using retention of 1.5, 2.0, 6.4 kg·m<sup>-3</sup> are compared at temperature (T) ranging from 70 °C to 50 °C and 5 different relative humidity (RH) conditions. The samples were investigated using the expressate method to follow chromium fixation. Red pine fixes faster than southern pine under all 11 post treatment schedules. The fixation rates for both species are not significantly different while the blocks were fixed under 6 fixation/drying schedules that differed only in the order of T/RH conditions applied. The rate of fixation of all samples in any fixation stage were reduced when the blocks were fixed under lower humidity conditions in spite of no change in chamber temperature. Some of this influence can be attributed to the effect of humidity on heat transfer into the wood and cooling of the wood surface.

**Keywords:** CCA-C, Fixation, Post treatment, Temperature, Relative humidity, Red pine, Southern pine

### Introduction

Waterborne preservatives are a major component of the wood-treating industry because of their ease of application, low cost, and the clean appearance of the wood after treatment. The use of chromated copper arsenate (CCA) preservatives in the USA has grown from a 14% share of the wood preservatives market in 1977 to 73% in 1987 (Micklewright 1993). This is mainly due to the increasing use of CCA-treated wood as decks and outdoor structures. The waterborne preservative CCA has become one of the most effective treatments for North American wood products, used in applications where the fungal and insect hazard is high (Boone *et al.* 1995; Cooper *et al.*; Micklewright 1993).

When the CCA solution is forced under pressure into wood, a series of complex chemical reactions take place, during which the active ingredients are fixed in the wood. The rate of this fixation process is strongly dependent on the fixation conditions of time, temperature and ambient relative humidity. A review of accelerated fixation of CCA-treated wood by Anderson (1989) indicates that fixation can also be accomplished by hot water spray or bath, steam, and hot oil. Recent work on CCA fixation mechanisms focuses on accelerated fixation at elevated temperature (Chen *et al.* 1994; Conradie & Pizzi 1987;

Cooper *et al.* 1989; Kaldas & Cooper 1996; Lee *et al.* 1993). Most CCA treating plant operators in Canada now use these systems for CCA treated products (Avramidis & Ruddick 1989; Boone *et al.* 1995; Lee *et al.* 1993; Ung. & Cooper 1996). Exposure of freshly treated wood to high temperature and humidity conditions results in rapid immobilization of the copper, chromium and arsenic components of the preservative.

Fixation is considered to be the state when all chemical reactions and interactions between the chemical and wood are completed. Properly fixed treated wood is at the highest stability with respect to leaching and other losses, and its highest levels of efficacy against decay organisms. CCA fixation can be monitored by several methods. Each has its own principles and is effective for specific situations. Cooper *et al.* (1993) summarized them as follows: 1) efficacy and leach resistance; 2) pH measurement; 3) quantitative determination of hexavalent chromium (Cr<sup>6+</sup>) in solution expressed from the wood void space; 4) qualitative detection of hexavalent chromium (Cr<sup>6+</sup>) by chromotropic acid; 5) quantitative measurement of total Cu, Cr, As or other preservatives components in solution expressed from wood; 6) electrical resistance (Cooper *et al.* 1993). Method 3 is a simple technique used by several treatment companies and research organizations using analysis of expressed solution for the monitoring of CCA fixation

Many have discussed the effects and interactions of ambient and wood temperature and relative humidity on fixation of CCA treated wood (Alexander *et al.* 1993; Avramidis & Ruddick 1989; Boone *et al.*

\* Visiting Associate Professor at the Faculty of Forestry, University of Toronto, Canada, from Inner Mongolia Forestry College, P.R China )

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1995; Chen *et al.* 1994; Kaldas & Cooper 1996; Lee *et al.* 1993; Ung. & Cooper 1996). Most of these studies represent a wide range of fixation/drying conditions but generally are performed under constant T/RH conditions within each study. The objective of this study was to specifically relate the effect of post-treatment combinations of dry / wet bulb temperature depressions on fixation rate in CCA treated red pine and southern pine.

## Materials and methods

### Experimental material

Samples of solid red pine (*Pinus resinosa* Ait.) sapwood were cut to dimension of 25 mm × 25 mm × 400 mm from 3.5-m long, 32-cm diameter red pine pole sections from Guelph Utility Pole Inc, Ontario Canada. Southern pine (*Pinus* spp) 38mm × 140mm × 250 mm long sapwood board segments were cut into 25 mm × 25 mm strips. The moisture contents (MC) of all samples were determined by the oven-drying method. Each strip was end- sealed with two coats of alkyd paint. All samples were conditioned to an equilibrium moisture content (EMC) of 12% at dry / wet bulb temperature = 35 °C / 31 °C in an enclosed chamber before CCA treatment.

### Preservative treatment

Twelve samples of each group were treated to achieve preservative retentions of 1.5, 2.0, 6.4 kg·m<sup>-3</sup>. The two low retention groups are lower than normal specifications and were prepared for subsequent soil block decay tests. The CCA solution used was type C (AWPA standard p5-98) (2) and had the following composition: 45.5 % CrO<sub>3</sub>, 18.5 % CuO, and 36% As<sub>2</sub>O<sub>5</sub>. The process consisted of an initial vacuum

period of 20 min at 24 in. Hg (20 kPa). A pressure period of 30 min at 90 psi (610 kPa) of pressure was then applied to make sure the sample would have the maximum absorption of preservative. Upon removal from the cylinder, the strips were immediately weighed to determine gross retention.

### Post-treatment

The choice of 70 °C and 50 °C as maximum and minimum dry-bulb temperatures for the study were based on previous work relating strength loss to maximum dry-bulb temperatures (Boone *et al.* 1995) and the fact that these are common temperatures used to accelerate fixation in most treatment plants. Each fixation schedule was divided into three stages of initial, middle and final fixation. Five levels of wet bulb depressions were selected for initial high humidity (or initial low humidity) and final low humidity (or final high humidity) under different periods of fixation. The fixation schedules used are summarized in Table 1. In schedules 1-3, samples were exposed to 50 °C and high humidity conditions for different times, to 60 °C and moderate drying (EMC=8%~9%) for a total time of 4 h for the first two conditions. Samples were then subjected to severe drying at 70 °C and 5.0% EMC conditions until chromium fixation was completed. Note that in all cases, the wet bulb temperature was approximately 50 °C. For schedules 4-6, the same dry bulb temperature were used, but the humidity (wet bulb) conditions were reversed so the more severe drying condition was at the start and the samples were exposed to high humidity at the end. For schedules 7-11, samples were exposed to constant conditions, representing each of the variable conditions used above.

**Table 1 Summary of post treatment schedules**

Schedule No.	First stage		Second stage		Third stage	
	D/W(°C)	Time /h	D/W(°C)	Time /h	D/W(°C)	Time /h
1	50/49	1	60/50	3	70/50	Until fixation is completed
2	50/49	2	60/50	2	70/50	
3	50/49	3	60/50	1	70/50	
4	50/38	1	60/50	3	70/68	is completed
5	50/38	2	60/50	2	70/68	
6	50/38	3	60/50	1	70/68	
7	50/38					
8	50/49					
9	70/50	Until fixation is completed				
10	70/68					
11	60/50					

25-mm (1 in) CCA chemical analysis blocks were cut from one end of each strip each half-hour during the fixation course. This wafer was squeezed in a

hydraulic press with a small aluminum pan to obtain expressate solution from wood for chemical analysis. The expressed liquid was analyzed for hexavalent

chromium ( $\text{Cr}^{16}$ ) by the diphenylcarbazide method with a Shimatzu uv 16 spectrophotometer (Cooper *et al.* 1993).

As the moisture content approaches the fiber saturation point, expressing of liquid becomes increasingly difficult. Vacuum treating the wood samples with water before expressing was done to provide enough solution for analysis. The water removed by drying could be replaced almost quantitatively (Alexander *et al.* 1993; Cooper & Ung. 1993; Kaldas & Cooper 1996).

## Results and discussion

### CCA preservative retention

The target retention for both red pine and southern pine was 1.5, 2.0 and 6.4  $\text{kg}\cdot\text{m}^{-3}$ . Calculated retention levels of these samples of 11 post treatment groups based on weight gain are shown in Table 2.

The retention of preservative solution affects fixation rate. With increasing retention in wood, fixation time also increased for a given fixation condition (Fig. 1, Table 2). Generally, per increasing retention of 1  $\text{kg}\cdot\text{m}^{-3}$ , fixation time increased 1-2 h at 50–70 °C and

low humidity; the time increased about 0.3-0.6 h per 1  $\text{kg}\cdot\text{m}^{-3}$  increase in retention at 50-70 °C and high humidity for red pine and southern pine blocks (Table 2).

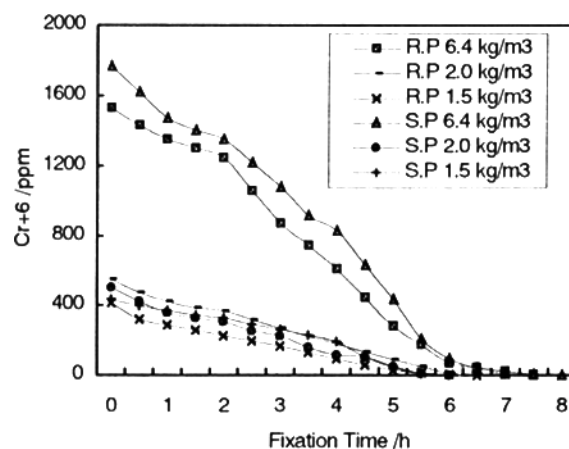


Fig. 1. Example of CCA retention effect on fixation rate

Table 2 Summary of actual retention and time to 99.9% fixation in Red pine and Southern pine

Schedule No	Wood Species	Actual retention / $\text{kg}\cdot\text{m}^{-3}$	Time to 99.9% Fixation /h	Actual retention / $\text{kg}\cdot\text{m}^{-3}$	Time to 99.9% Fixation /h	Actual Retention / $\text{kg}\cdot\text{m}^{-3}$	Time to 99.9% Fixation /h
Target Retention:		6.4		2.0		1.5	
1	Red Pine	7.1	7.5	2.2	6.0	1.6	5.0
	Southern Pine	7.4	8.8	2.4	6.5	1.5	5.5
2	Red Pine	7.2	7.5	2.2	6.0	1.6	5.0
	Southern Pine	7.2	7.5	2.4	6.5	1.9	6.0
3	Red Pine	7.5	8.0	1.9	5.5	1.8	5.5
	Southern Pine	6.8	7.5	2.4	6.5	1.9	6.0
4	Red Pine	6.8	7.5	2.1	5.8	1.6	5.5
	Southern Pine	6.8	8.0	1.9	6.0	1.5	5.5
5	Red Pine	6.4	6.5	2.1	5.8	1.3	5.0
	Southern Pine	7.2	8.0	1.9	6.0	1.6	6.0
6	Red Pine	7.4	7.7	2.3	6.0	1.7	5.5
	Southern Pine	6.7	7.0	2.2	6.0	1.9	6.0
7	Red Pine	6.7	18.2	2.3	14.0	1.7	13.0
	Southern Pine	6.4	22.8	2.4	16.0	1.8	15.0
8	Red Pine	6.2	11.0	1.9	9.0	1.6	8.0
	Southern Pine	6.8	14.5	2.2	10.0	1.6	9.0
9	Red Pine	6.7	7.0	2.3	5.5	1.7	4.5
	Southern Pine	7.0	8.0	2.2	5.5	1.7	5.0
10	Red Pine	6.9	3.5	2.1	2.5	1.6	2.5
	Southern Pine	7.0	4.0	2.9	2.5	1.7	2.0
11	Red Pine	6.5	8.5	2.0	6.0	1.5	5.0
	Southern Pine	7.7	10.0	2.4	6.5	1.9	6.0

### Effect of species

In most fixation/drying schedules (schedules 1-6), fixation time of the southern pine samples at three CCA retention were slightly longer than red pine at the same fixation /drying conditions (Table 2).

### Fixation rate

Fixation is a multiple-path chemical process of rendering the water-soluble preservative elements insoluble and, therefore, resistant to removal from the wood (Alexander *et al.* 1993; Avramidis *et al.* 1989;

Conradie & Pizzi 1987). Although fixation is not fully understood, it is sometimes defined as the point when hexavalent chromium is no longer detectable and has primarily been reduced to  $\text{Cr}^{+3}$  (Cooper *et al.* 1993a, 1993b; Lee *et al.*; Lebow *et al.* 1996). Complete reduction of the chromium indicates that the potential for copper and arsenic leaching has been minimized (Boone *et al.* 1995; Cooper *et al.* 1989). So measuring and analyzing the reduction of hexavalent chromium can reflect the fixation rate of CCA treated wood. Fig. 2 shows an example of the rate of drop of  $\text{Cr}^{+6}$  content on the expressate and the corresponding % fixation for schedule 9. The time to fixation from start (about 30%~40%) to about 85% fixation is approximately the same as to go from 85%~97% or from 97% to 99.9% fixation for retentions of 1.5-2.0  $\text{kg}\cdot\text{m}^{-3}$ . For high retention (6.4  $\text{kg}\cdot\text{m}^{-3}$ ), the time from start to 80% fixation is approximately the same as to go from 80%~95% or 95%~99.9%. From the general result, the beginning of the fixation period appears to be most important to fix preservative to wood components, because about 60%~80% chemical elements were fixed in that period. If the preservative solution can permeate better into cell walls and be not deposited on the surface of cell lumens earlier, leaching losses of chemical elements may be reduced after treatment.

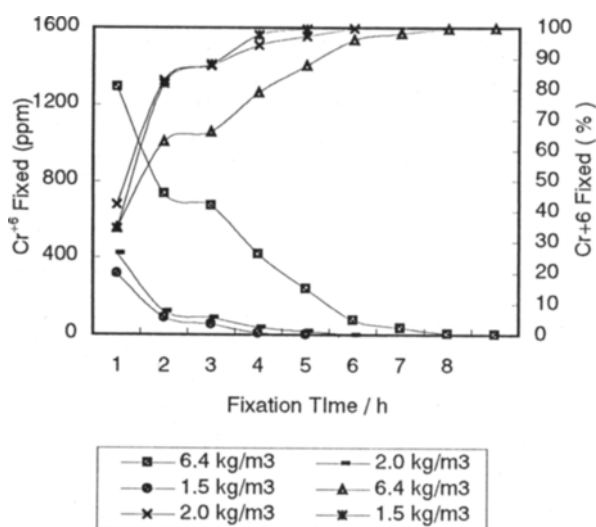


Fig. 2. Example of the relationship between chromium reduction in expressate and % fixation

#### Effect of fixation conditions

Schedules 1, 2 and 3 start with high humidity conditions and end with drying conditions while schedules 4, 5, and 6 reverse these conditions. Schedule 1 and 4, 2 and 5, and 3 and 6 are identical except that the order of T/RH conditions is reversed (Table 3). The effect of the order of fixation conditions can best be seen in Fig. 3 and 4. Initial exposure to high humidity

(Fig. 3) results in rapid initial fixation rate because the wood reaches the relatively high wet bulb temperature quickly. Fixation conditions initially at the same dry bulb temperature but under drying conditions (Fig. 4) have a much slower initial fixation rate due to evaporative cooling of the wood surface in the dry environment, causing the wood to reach the much lower wet bulb temperature. In contrast, at the ends of the fixation schedule, samples exposed to schedule 1 to 3 fix more slowly at the end because of the low humidity conditions, and those exposed to high humidity conditions maintain a more constant fixation rate over the entire schedule. However, the net effects in all cases are similar: total fixation time of approximately 7.5 h for red pine and 7.8 h for

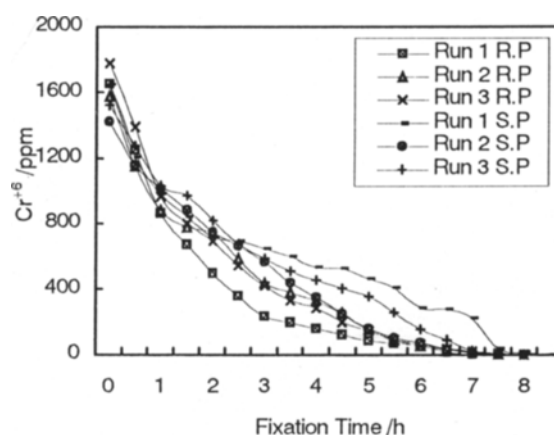


Fig. 3. Red pine (R. P) and Southern pine (S.P) fixed at schedule 1-3 for 6.4  $\text{kg}\cdot\text{m}^{-3}$

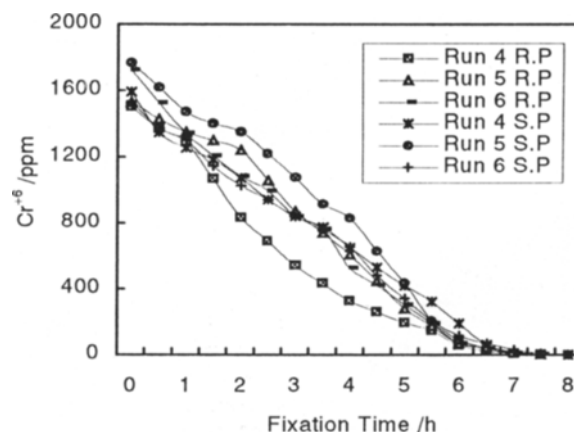


Fig. 4. Red pine (R. P) and Southern pine (S.P) fixed at schedule 4-6 for 6.4  $\text{kg}\cdot\text{m}^{-3}$

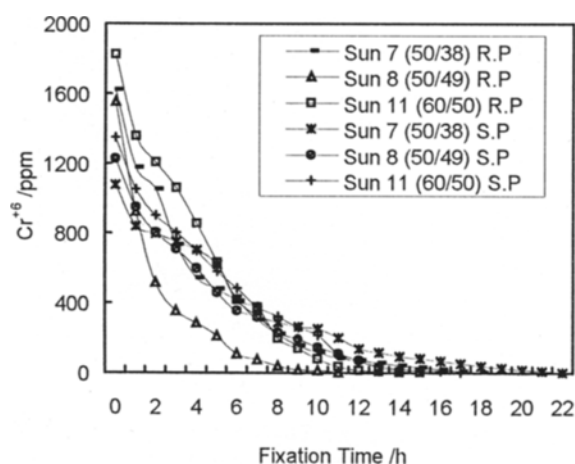
Southern pine. Samples fixed at 70/68 °C or 70/50 °C had completed chromium reduction 3-4 times faster than those fixed at 50/48 °C or 50/38 °C for

both red pine and southern pine (Table 2, Fig. 5-6). Fixation times were significantly reduced at high temperature, whatever the humidity conditions. For example, fixation time was 3.5 h for schedule 10 (70/68 °C), and 11 hours for schedule 8 (50/49 °C) for red pine at 6.4 kg.m<sup>-3</sup>. For southern pine, fixation time was 4.0 h at 70/68 °C, 14.5 h at 50/49 °C. At 20 °C, both species require over two weeks to achieve the same degree of fixation as those reported here (Cooper *et al.* 1989). The rates of fixation are significantly inhibited if the wood is allowed to dry excessively during the fixation process (Conradie & Pizzi 1987). This is evident in schedules 7 (50/38 °C), 9 (70/50 °C) and 11 (60/50 °C) in Fig. 5 and 6. Comparing fixation by schedule 7 (50/38 °C) or schedule 9 (70/50 °C) with schedule 8 (50/49 °C) or schedule

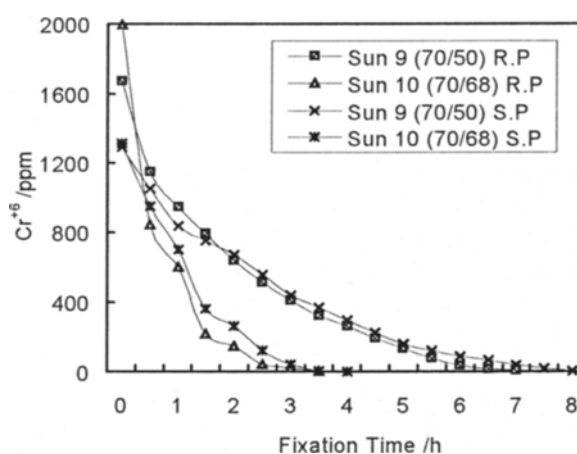
10 (70/68 °C) for both species, fixation time increased almost 50 % for 6.4 kg.m<sup>-3</sup> for the lower humidity conditions. For low retentions (1.5, 2.0 kg.m<sup>-3</sup>), the fixation time increased by 30%~50% at the low RH conditions. From these results it can be seen that fixation rate is significantly dependent on humidity. While the effect is usually attributed to impaired diffusion and reaction of preservative components during simultaneous drying and fixation, much of the effect can be explained by heat transfer (Alexander *et al.* 1993; Boone *et al.* 1995; Conradie & Pizzi 1987). The rates of heat transfer and CCA fixation are substantially influenced by the cooling effect of water evaporating from the wood surface when drying occurs during fixation (Ung. & Cooper 1996).

**Table 3. Comparison of fixation rate at two different fixation / drying conditions**

Schedule No.	Initial Fixation			Middle Fixation			Final Fixation		
	D/W (°C)	Time /h	Avg Cr <sup>+6</sup> % / h	D/W (°C)	Time /h	Avg Cr <sup>+6</sup> % / h	D/W (°C)	Time /h	Avg Cr <sup>+6</sup> % / h
Red Pine									
1	50/49	1	786	60/50	3	263	70/50	3.5	44
2	50/49	2	416	60/50	2	207	70/50	3.5	91
3	50/49	3	453	60/50	1	135	70/50	4.0	81
4	50/38	1	212	60/50	3	322	70/68	3.5	93
5	50/38	2	143	60/50	2	318	70/68	2.5	173
6	50/38	3	293	60/50	1	315	70/68	3.7	150
Southern Pine									
1	50/49	1	665	60/50	3	149	70/50	4.8	118
2	50/49	2	353	60/50	2	199	70/50	3.5	87
3	50/49	3	310	60/50	1	132	70/50	3.5	113
4	50/38	1	339	60/50	3	201	70/68	4.0	144
5	50/38	2	206	60/50	2	262	70/68	4.0	184
6	50/38	3	232	60/50	1	182	70/68	3.0	164



**Fig. 5. Red pine (R. P) and Southern pine (S.P) fixed at schedule 7-8 for 6.4 kg m<sup>-3</sup>**



**Fig. 6. Red pine (R. P) and Southern pine (S.P) fixed at schedule 9-10 for 6.4 kg m<sup>-3</sup>**

These results are consistent with those observed by other research scientists (Avramidis and Ruddick 1989; Kaldas & Cooper 1996; Ung. & Cooper 1996), and can be summarized as follows: 1) The wood surface temperature under drying condition approaches the wet bulb temperature in the chamber, not the dry bulb temperature or ambient temperature. Thus, at a given dry bulb temperature, the wood surface temperature is lower at lower relative humidity and the rate of heating is reduced. 2) The cooling effect of surface evaporation of water under drying conditions, results in the effective fixation temperature being the wet bulb temperature rather than the dry bulb temperature of the fixation chamber (at least in initially and middle fixation). 3) Under low humidity conditions, the heat capacity of the chamber (or kiln) air is lower and convective heat transfer to wood surface is lower. 4) The wood surface equilibrates to the EMC which is below the fiber saturation point which interferes with fixation and reaction of the CCA components. 5) Maintaining a high humidity facilitates maximum rate of heat transfer into the wood and also prevents wicking of unfixed CCA components to the wood surface during fixation process. In further studies, we will evaluate the leaching and decay susceptible performance of samples exposed to the above fixation conditions.

## Conclusions

Red pine (*Pinus resinosa* Ait.) and southern pine (*Pinus* spp.) samples were treated with CCA-C at retention of 1.5, 2.0 and 6.4 kg·m<sup>-3</sup> and allowed to fix under 50-70 °C and different relative humidity conditions (11 post treatment schedules). The blocks were evaluated for rate of chromium fixation by determining the residual unreacted chromium in expressate at different times after treatment.

Red pine fixed slightly faster than southern pine and the times to complete chromium fixation for both species are variable. The rate of CCA-C fixation is highly temperature dependent with relative humidity or wet bulb temperature playing an important role in fixation performance. For example, ranging from 3.5 hours at 70/68 °C to 18.5 h at 50/38 °C for red pine at retention of 6.4 kg·m<sup>-3</sup>, and from 4.0 h to 22.8 h for southern pine in the above conditions. There were slight variations in fixation times under 6 fixation/drying schedules ranging from 6.5–8 h for red pine, from 7.0–8.8 h for southern pine at 6.4 kg·m<sup>-3</sup>. Lower retention treatments resulted in slightly faster fixation, from 5.0–6.5 h for both species at 1.5 and 2.0 kg·m<sup>-3</sup>.

## References

- Alexander, D.L., Ung, T.Y., Cooper, P.A. 1993. Effects of temperature and humidity on CCA-C fixation in pine samples. *Wood Protection*, **2**(2): 29-45
- American Wood Preservers' Association. 1997. The AWP Book of Standards, AWP, Woodstock, MD
- Anderson, D.G. 1989. The accelerated fixation of chromium copper preservative treated wood. *Proc. Can. Wood Preserv. Assoc.*, **10**: 75-110
- Avramidis, S., and Ruddick, J.N.R. 1989. Effect of temperature and moisture on CCA fixation. *Holz-als , Roh- und Werkstoff*, **7**(8): 328
- Boone, R.S., Winandy, J.E. 1995. Effects of redrying schedules on preservative fixation and strength of CCA-treated lumber. *Forest Prod. J.*, **45**(9): 65-73
- Chen, J.M., Kaldas, M., Ung, T.Y., Cooper, P.A. 1994. Heat transfer and wood moisture effects in moderate temperature fixation of CCA treated wood. IRG/WP/40022, 13pp
- Conradie, W.E., and Pizzi, A. 1987. Progressive heat inactivation of CCA biological performance. *Proc. Amer. Wood Preserv Assoc.*, **83**:32-49
- Cooper, P. A., Alexander, D.L., and Ung, Y.T. 1993a. What is chemical fixation ? In: chromium-containing waterborne wood preservatives, fixation and environmental issues. *Forest Prod Soc, Madison, Wis*, pp 7-13
- Cooper, P.A., and Ung., T.Y. 1993b, A simple quantitative measure of CCA fixation. *Forest Prod. J.*, **43**(5): 19-20
- Cooper, P.A., Ung., T.Y. and Leonov, E. 1989. Fixation of CCA-C treated pine at moderate temperature. *Proc. Can Wood Preserv. Assoc.* **10**:111-118
- Kaldas, M. and Cooper, P. A. 1996. Effect of wood moisture content on rate of fixation and leachability of CCA-treated red pine. *Forest Prod. J.*, **46**(10): 67-71
- Kartal S. Nami. 1999. The leachability, biological resistance and mechanical properties of wood treated with CCA and CCB preservatives. 1999, IRG /WP/99-30207
- Lee, A.W.C., Grafton, J.C. and Tainter, F.H. 1993. Effect of rapid redrying shortly after treatment on leachability of CCA-treated southern pine. *Forest Prod. J.*, **43**(2): 37-40
- Lebow, S.T., Morrell, J.J., and Milota, M.R. 1996. Western wood species treated with chromium copper arsenic: Effect of moisture content. *Forest Prod. J.*, **46**(2): 68-70.
- Micklewright, J.T. 1993. Wood preservation statistics 1991. A report to the wood preserving industry in the USA. American Wood Preservers' Assoc. Woodstock. MD. 11pp
- Smith, P.M. and Sinclair, S.A. 1990. The professional contract / remodeler: Marker research for CCA-treated lumber products. *Forest Prod. J.*, **40**(6): 8-14
- Ung, T.Y., and Cooper, P.A. 1996. Feasibility of drying CCA-treated red pine poles during fixation. *Forest Prod.*, **46**(6):46-5